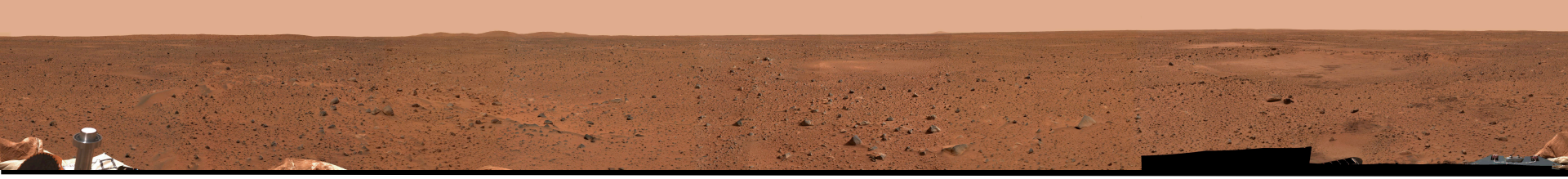


Microfabricated Organic Analyzer (MOA) for *in situ* Exploration of Mars and other Solar Bodies

- Prof. Richard A. Mathies, Chemistry Department, UC Berkeley, microfabricated devices and biochemical analysis

- Prof. Jeff Bada, Scripps Institution of Oceanography, UCSD, amino acid analysis and astrobiology

- Dr. Frank Grunthaner, Jet Propulsion Laboratory, instrument design, operation and flight engineering

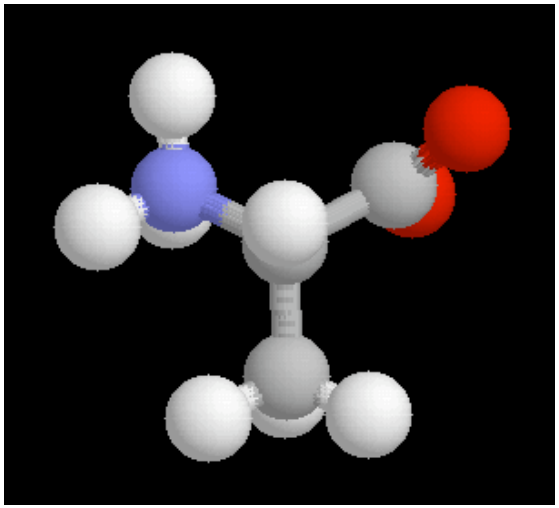
Project Goals

- Complete brass-board development of microfabricated capillary electrophoresis (CE) chip and instrument for amino acid analysis
- Integrate the microchip CE system with MOD sampling system to form the Mars Organic Analyzer (MOA)
- Perform field tests of the MOA in Mojave and three Mars-like Atacama sites
- Document maturation, integration and field operation of two MIDP, PIDDP and ASTID-derived instruments
- Enhance TRL of MOA through Mojave and Atacama field testing
- Increase our understanding of limits and constraints of life in extreme environments
- Critically define identity of and sensitivity requirements of potential biomarkers.

Amino Acid Composition and Chirality Analysis

Potential bioorganic signatures:

- **Large biomolecules likely degraded by oxidizing surface environment of Mars**
- **Amino acids have a longer lifetimes in dry, harsh conditions**
- **Amino acids have been found in meteorites**
- **Amino acid chirality is indicative of origin:**
- **Racemic mixture – abiotic origin**
- **Non-racemic mixture – biological origin**



L-alanine

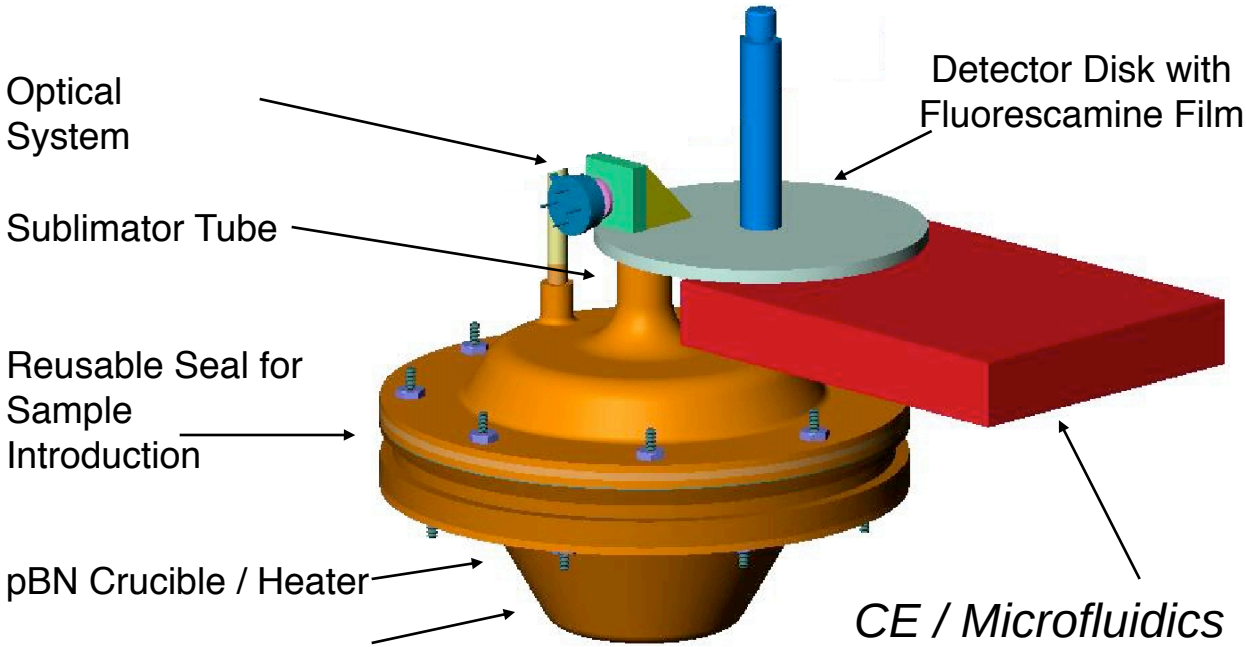
Why *in situ* analysis:

- **Significant contamination of Meteorites found on earth by terrestrial sources of life**
- **Sample return missions are more technologically challenging, costly and time consuming**

Allan Hills Meteorite

Mars Organic Analyzer (MOA) Concept

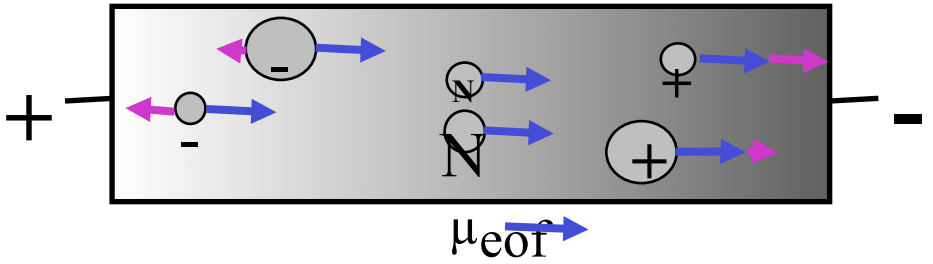
- **Soil samples collected and deposited into Mars Organic Detector (MOD)**
- **MOD sublimes amino acids onto cold finger coated with fluorescamine[1]**
- **Fluorescamine-labeled amino acids analyzed for composition and chirality via microchip Capillary Electrophoresis**



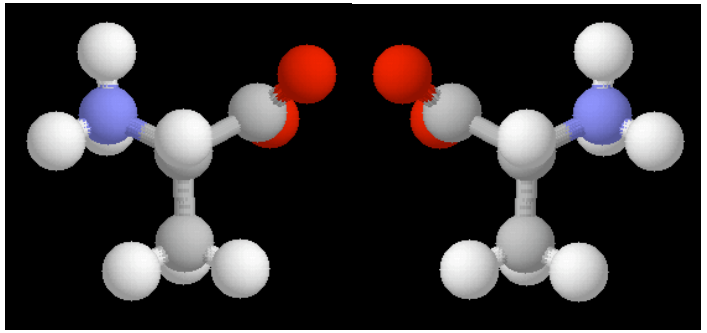
[1] Kminek, et al., *Planetary & Space Science* 2000, *48*, 1087-1091.

Composition and Chirality Analysis by CE

- **Electroosmotic flow (EOF) sweeps all molecules to the cathode**

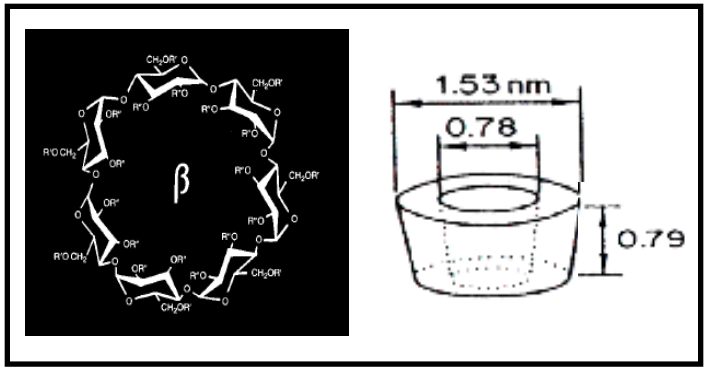


- **CE separates amino acids based on charge/size ratio giving composition information**



L-alanine **D-alanine**

- **Cyclodextrins included in running buffer provide enantiomeric resolution of amino acids**

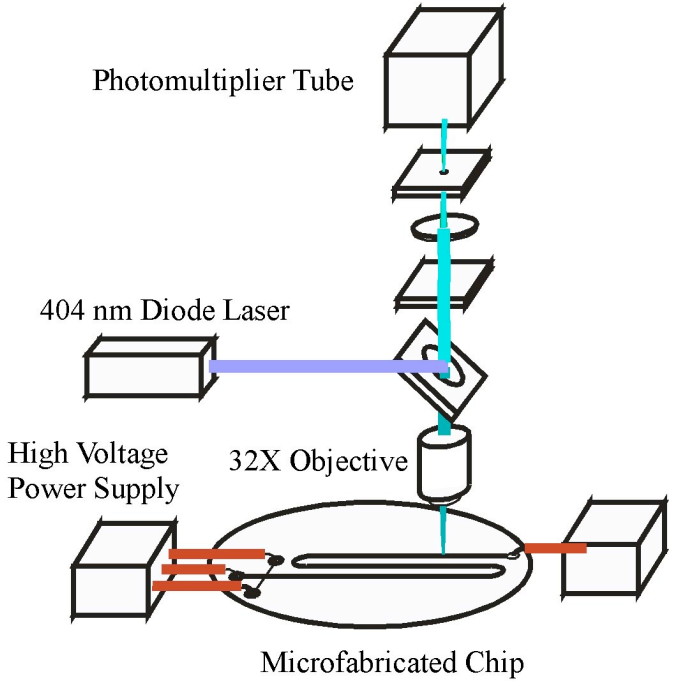


g-cyclodextrin

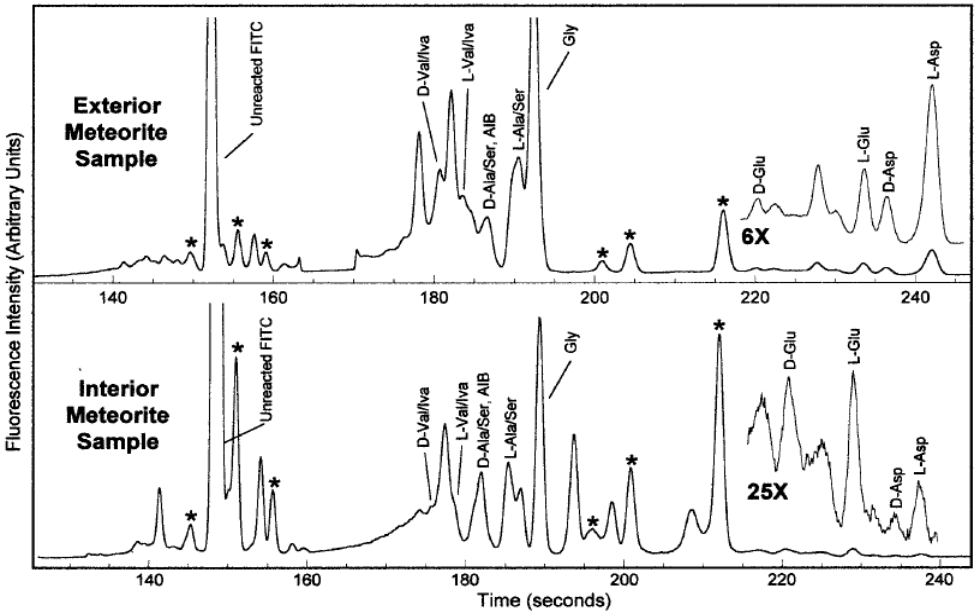
L-aa + CD => L-complex (K_L)
D-aa + CD => D-complex (K_D)

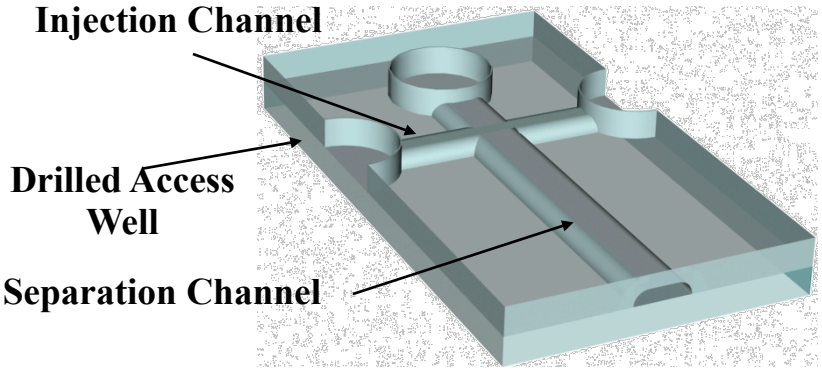
$$K_L \neq K_D$$

Established Separation and Lab-Based Detection System



Analysis of Fluorescein-labeled Amino Acids





Murchison Meteorite Glu and Asp D/L values

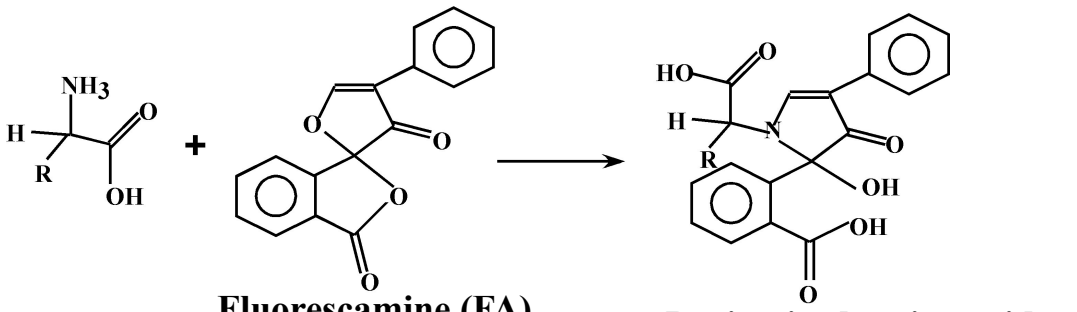
Amino Acid	HPLC	Microchip CE
Glu		
Exterior	0.3 – 0.1	0.33 + 0.04
Interior	0.7 – 0.1	0.65 + 0.07
Asp		
Exterior	0.3 – 0.1	0.21 + 0.03
Interior	0.3 – 0.1	0.30 + 0.06

Hutt, L. D.; Glavin, D. P.; Bada, J. L.; Mathies, R. A. *Analytical Chemistry* 1999, *71*, 4000-4006.

Separation of Fluorescamine-labeled Amino Acids

Advantages of Fluorescamine:

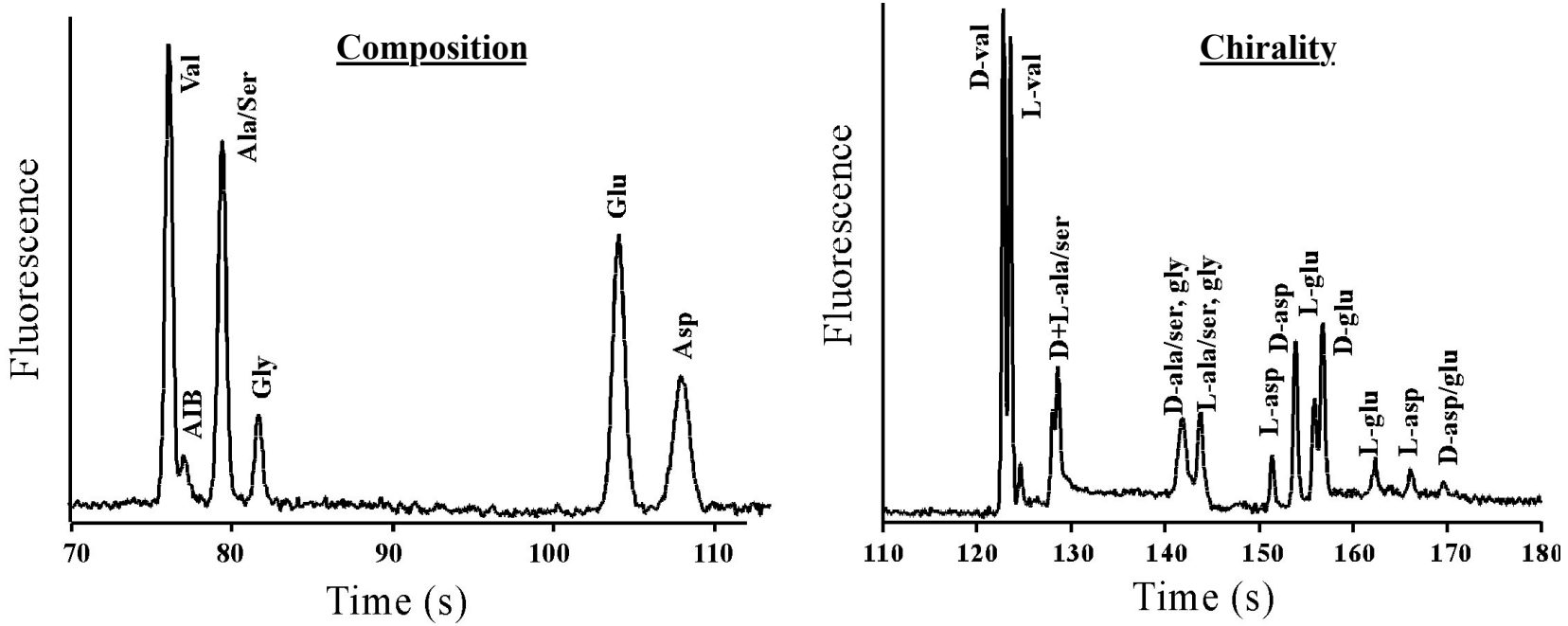
- **Fluorogenic reagent**
- **Reaction time ~1 min**
- **~ 50 nM LOD attainable**
- **Reagent used in MOD**



Fluorescamine (FA)

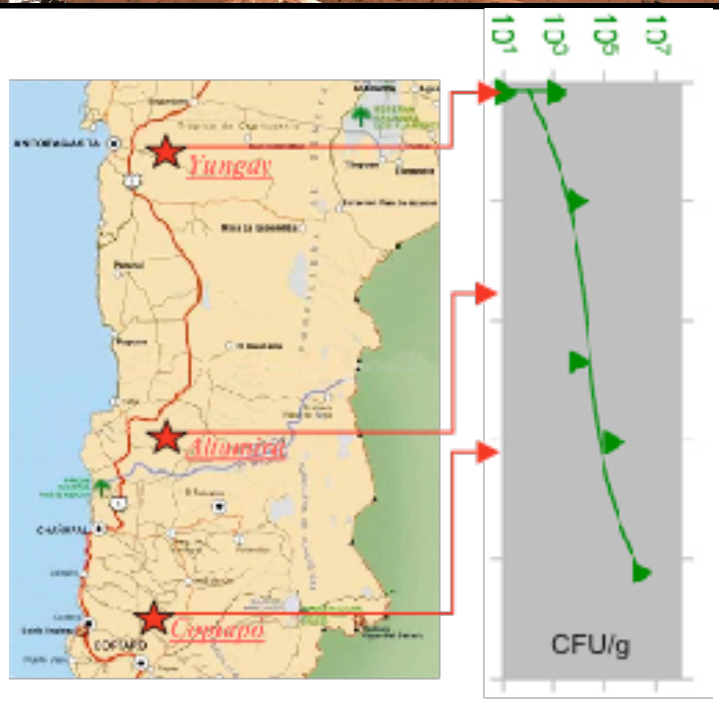
Derivatized amino acid (absorption max @ 390 nm)

Separation of Mars 7 Standard labeled with Fluorescamine



A. M. Skelley and R. A. Mathies, *J. Chromatogr. A* 2003, *1021*, 191-199.

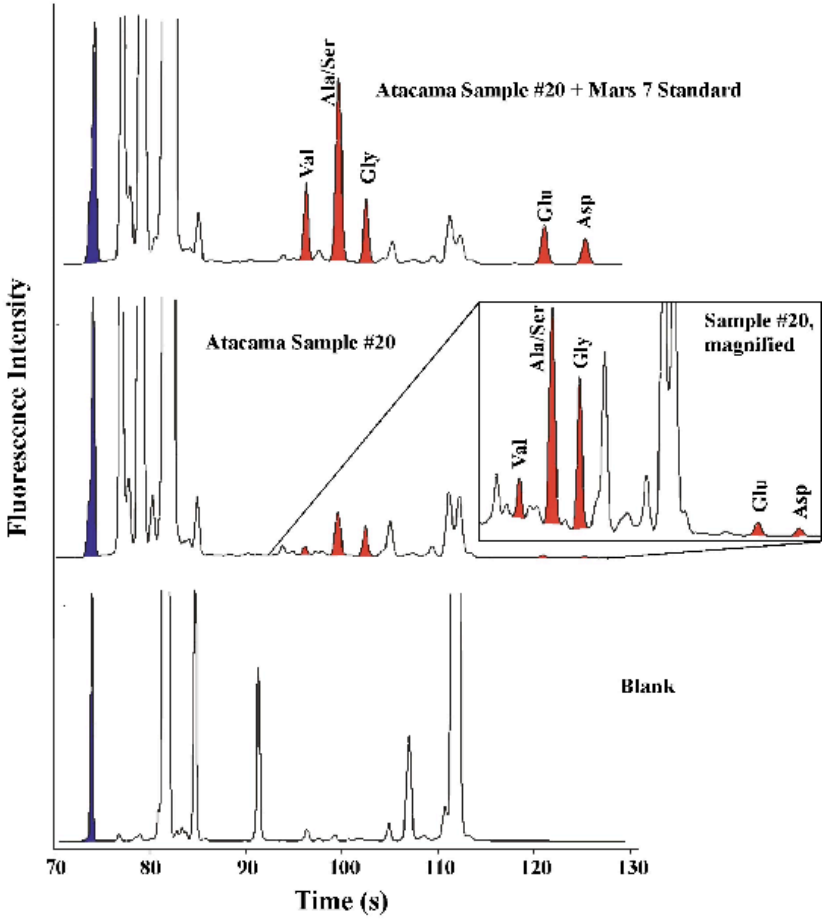
Atacama Desert as Martian Analog Site



- **Chilean Atacama Desert is one of the driest sites on the planet (<0.5 mm H_2O/year).**
- **The transect from Lat 24˚ to 28˚ South at 69.5˚ West has been extensively studied.**
- **Some areas have unusual surface oxidation chemistry and organic soil concentrations at lab blank levels. Other areas show readily detected microbial and higher life forms.**

Analysis of Atacama Soil Extracts

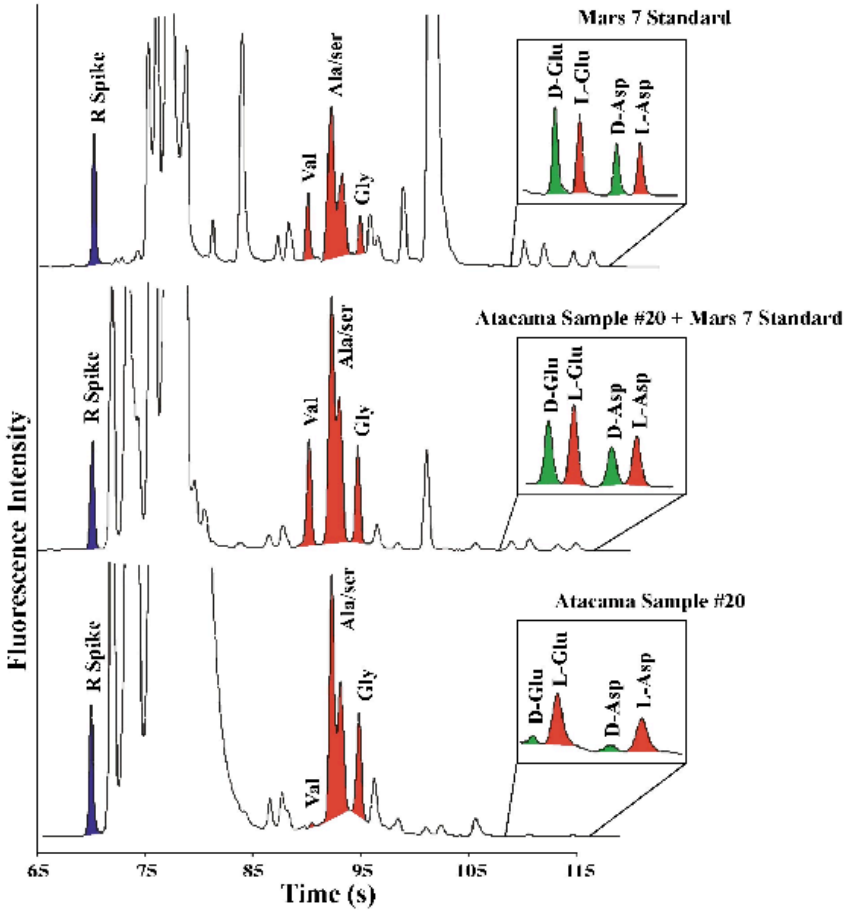
Composition



Blank-corrected Concentrations (weight/weight):

Val = 0.034 ± 0.009 ppm	Ala/ser = 0.32 ± 0.07 ppm
Gly = 0.18 ± 0.03 ppm	Glu = 0.14 ± 0.02 ppm
Asp = 0.094 ± 0.004 ppm	

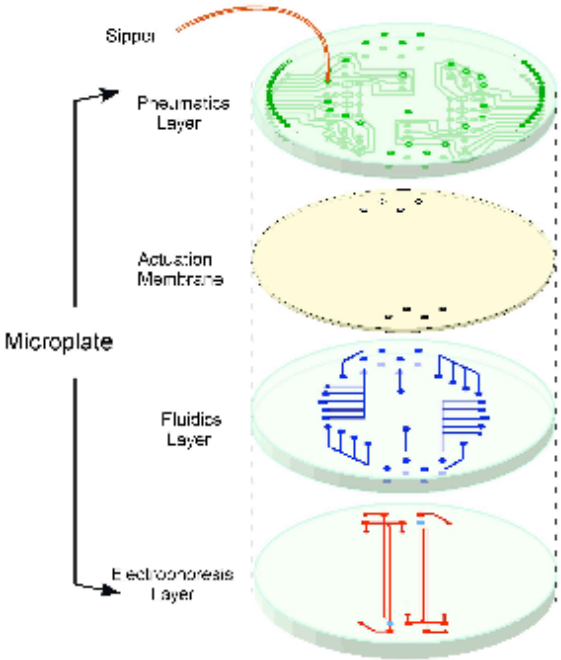
Chirality

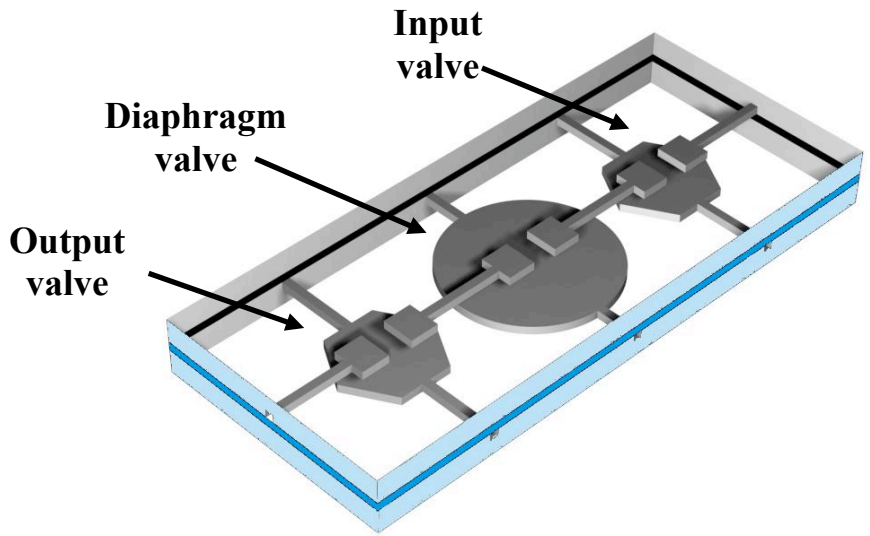


Blank-corrected Enantiomeric Ratios:

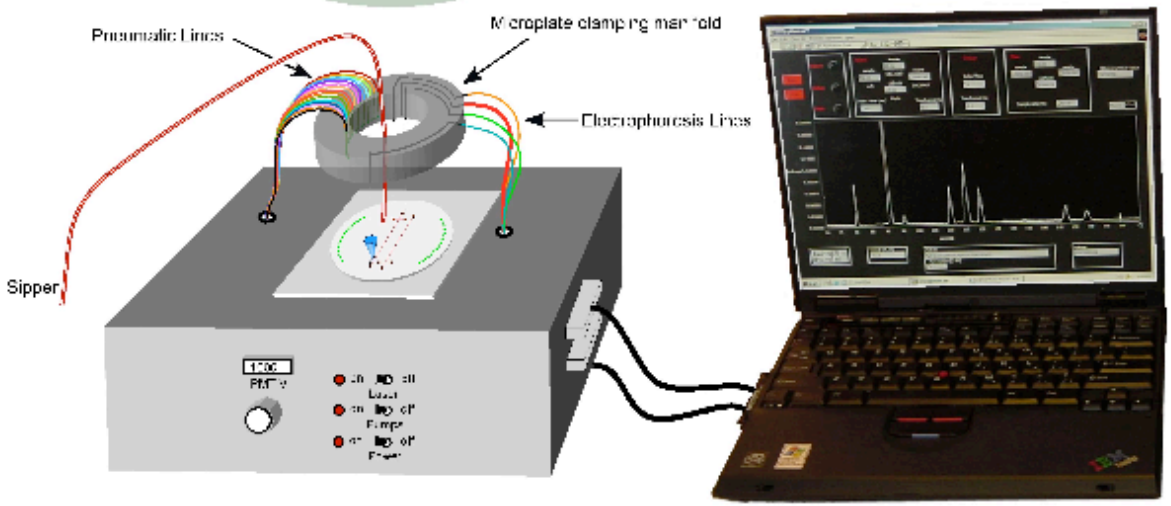
Mars 7 Standard:	**Atacama Sample # 20**
D/L Glu = 1.10 ± 0.02	**D/L Glu = 0.22 ± 0.02**
D/L Asp = 0.97 ± 0.02	**D/L Asp = 0.16 ± 0.02**

Portable Microchip CE System - Schematic





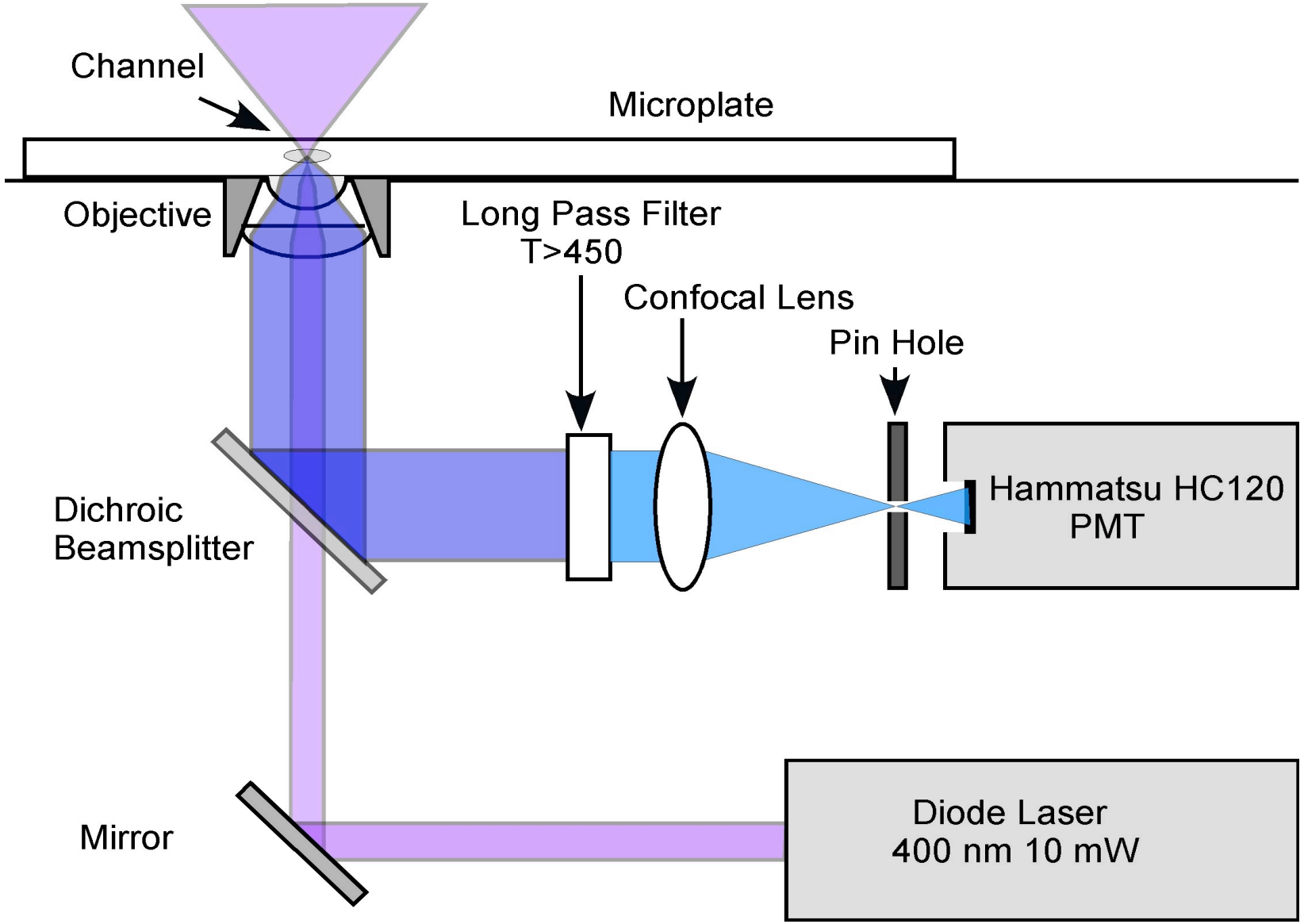
W.H. Grover, A.M. Skelley, C.N. Liu, E.T. Lagally, R.A. Mathies, *Sens. Actuators B* 89 (2003) 325.



Berkeley, UCSD and JPL

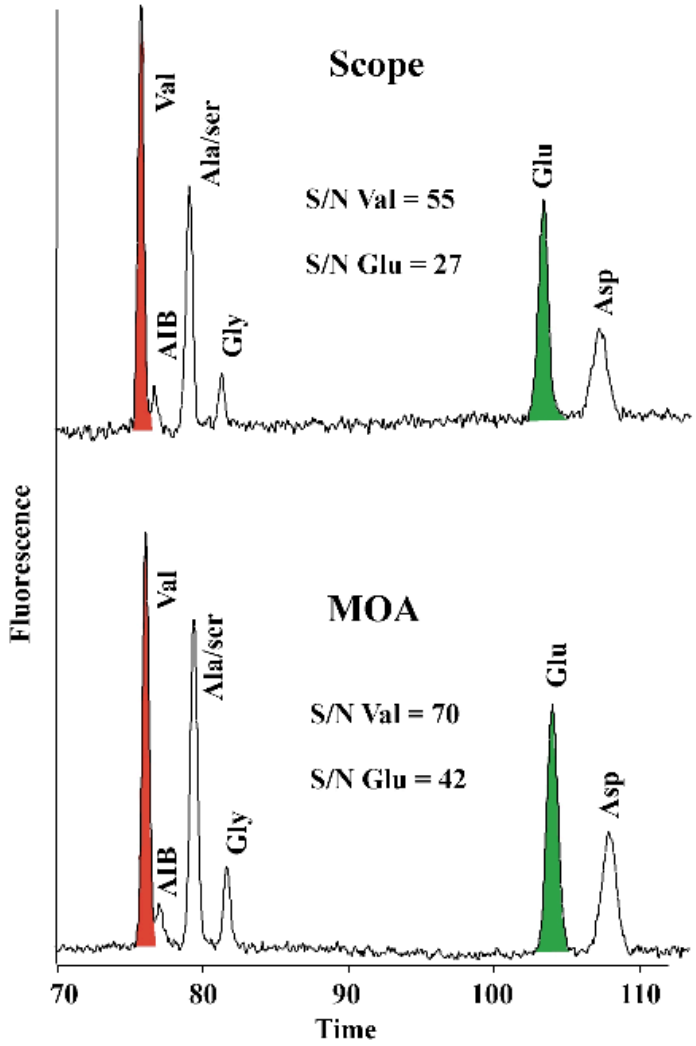
Mars Organic Analyzer (MOA)

Portable Microchip CE Instrument

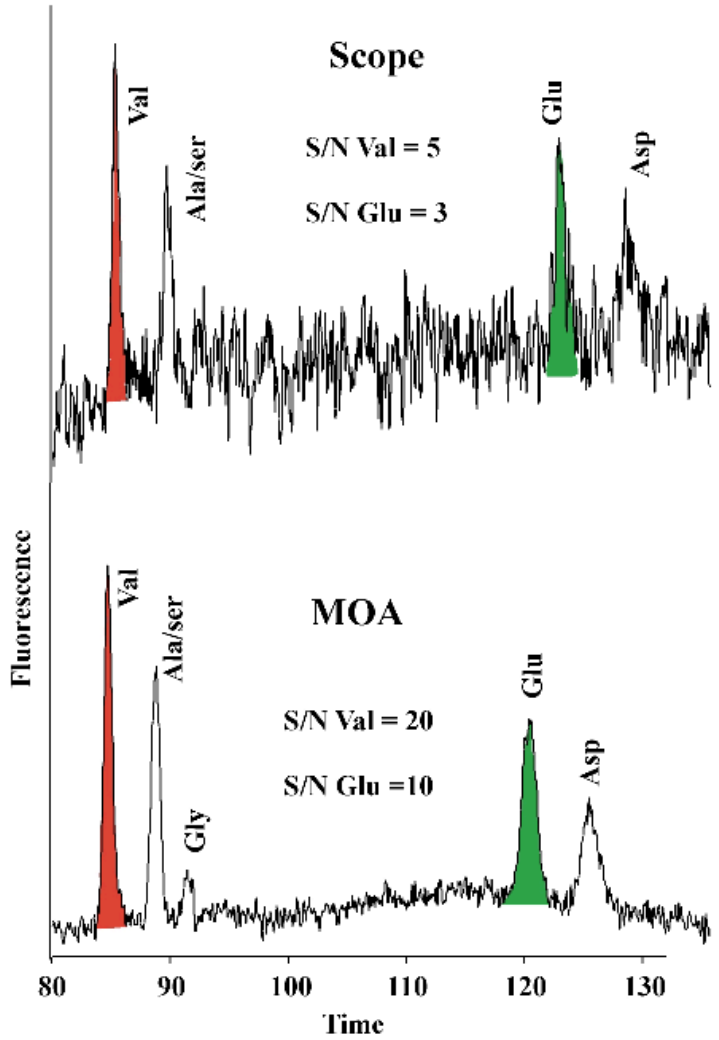


Comparison of Lab and MOA Systems

Concentration of each AA = 2.2 mM

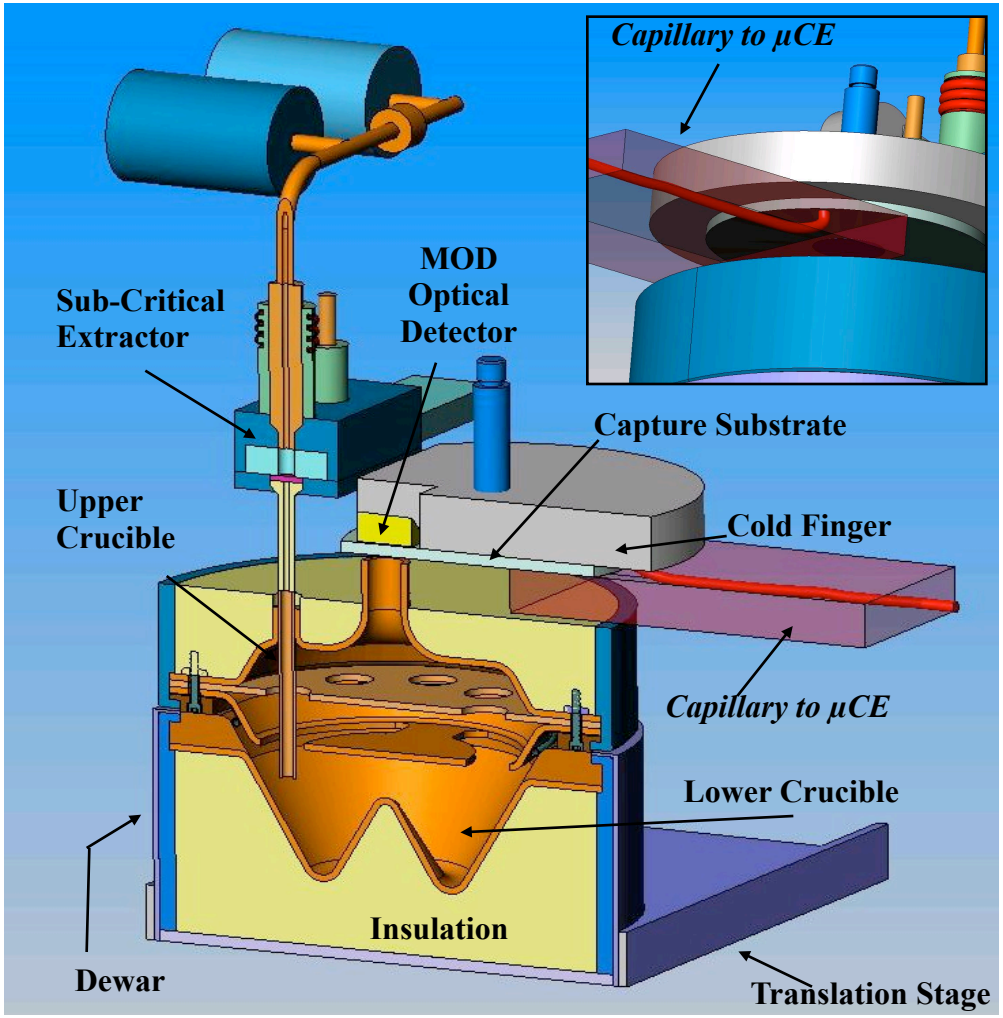


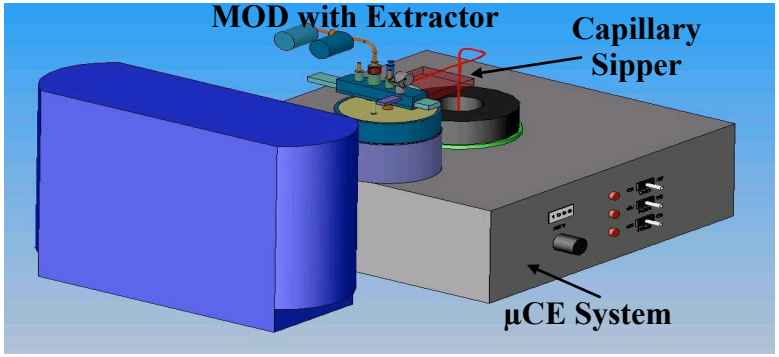
Concentration of each AA = 444 nM

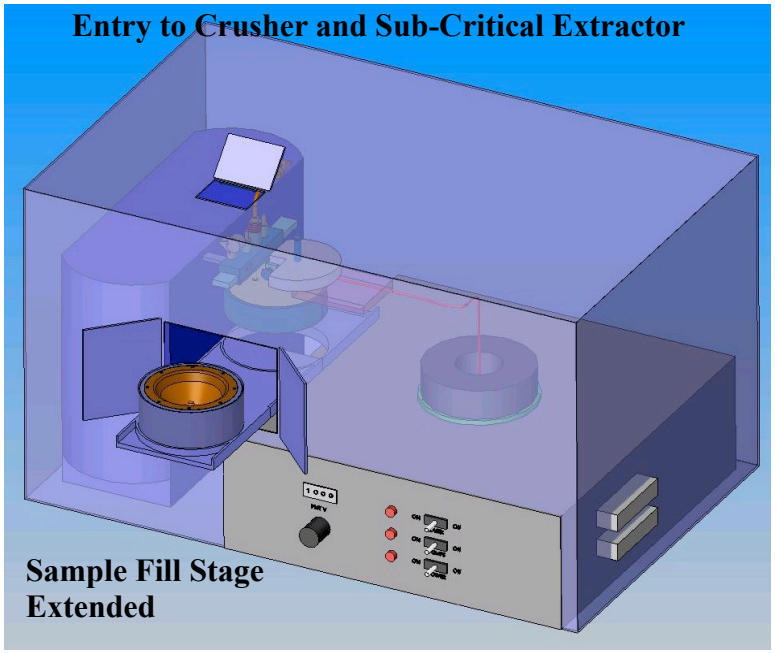


- **MOA system shows superior sensitivity and comparable separation efficiency**

MOD + CE = MOA


Capillary to µCE
MOD
Optical
Detector
Sub-Critical
Extractor
Capture Substrate
Upper
Crucible
Cold Finger
Capillary to µCE
Lower Crucible
Insulation
Dewar
Translation Stage


MOD with Extractor
Capillary
Sipper
µCE System


Entry to Crusher and Sub-Critical Extractor
Sample Fill Stage
Extended

Summary

- **Amino acid composition and chirality is an ideal means for organic biomarker detection on Mars.**

- **Microfabricated CE instrument provides a demonstrated means for sensitive amino acid composition and chirality analysis.**

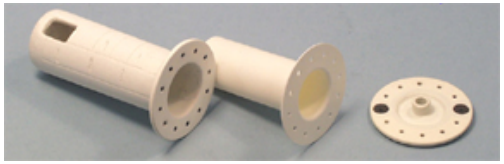
- **Portable CE instrument has identical separation efficiency and greater sensitivity than standard lab systems.**

- **Integration of CE with MOD to make MOA will provide sensitive analysis of amino acids in Martian soil.**

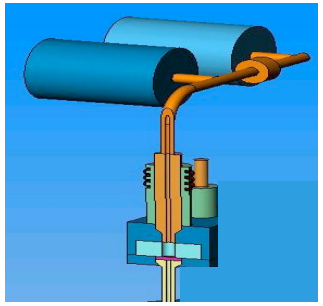
- **Field tests in Mojave and Atacama Deserts are planned as a critical test of technology readiness and analysis capabilities.**

- **Microchip is a powerful platform for preparation other analytes from other sources for many types of analyses.**

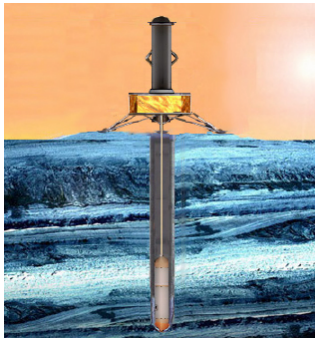
Mars Organic Laboratory (MOL): Beyond amino acids



MOD

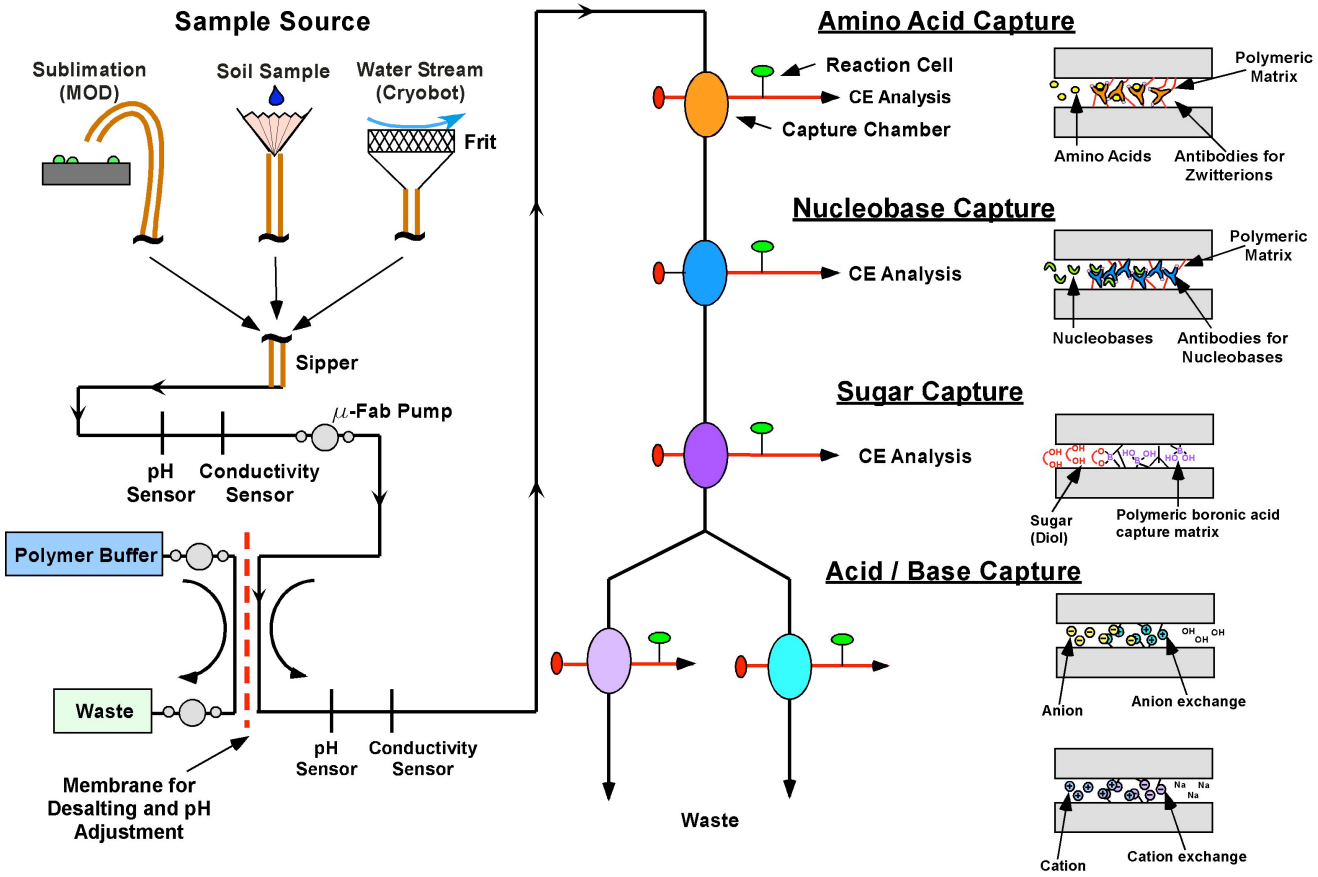


Sub-Critical Extractor



Cryobot

MOL Schematic - ASTID Project



1. A.M. Skelley et al., *SPIE: Proceedings of the In-Situ Instrument Technologies Meeting*, 4878 (2002) 59.
2. E.T. Lagally et al., *Lab-on-a-Chip*, 1 (2001) 107. Integrated PCR with CE analysis of nucleic acids
3. E.T. Lagally et al., *Anal. Chem*, submitted (2004). Portable bacterial detection and typing instrument

Acknowledgements

- Alison Skelley, Jim Scherer and Will Grover
- ASTEP - *Microfabricated Organic Analyzer (MOA) for in situ Exploration of Mars and Other Solar Bodies* PI's Mathies, Grunthaner and Bada, 1/04 -1/07.
- ASTID - *Integration of a Micro-chip Amino Acid Chirality Detector into the Mars Organic Detector,* subcontract to UCB from UCSD, PI Bada, 5/02 - 5/04.
- JPL Instrument Development Funds
- NSERC Fellowship to Alison Skelley
- UC Berkeley Microfabrication Laboratory